Numerical Analysis of the Piezoelectric Photothermal Spectra of $Cd_{1-x}Mn_xTe$ Mixed Crystals – Multilayer Approach.

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Abstract

In this paper a numerical analysis of the piezoelectric photothermal (PPT) spectra of a series of $Cd_{1-x}Mn_xTe$ mixed crystals are presented. The results indicated that the investigated mixed crystals exhibited non-uniform composition being the result of diversified spatial distribution of manganese ions in the samples. Computations of the piezoelectric spectra were performed for multi-layer models of real samples. The percentage compositions of crystals were determined, in the two crystal regions approach, and the types of spatial distribution of manganese in the samples were revealed. The numerical analysis explained also the origin of the peaks observed in the amplitude PPT spectra.

I .Introduction.

Piezoelectric photothermal (PPT) spectroscopy enables determination of several basic optical and thermal parameters of semiconductor materials. It can be especially useful in the analysis of mixed crystals. In recent years from the qualitative method it has become a quantitative one and now when both the amplitude and phase spectra are computed the precise analysis of the structure of the spectra became possible. Computations of the spectra not only enabled extraction of a series of basic thermal and optical parameters of samples but also revealed the complex physical structure of samples i.e. their inhomogeneous composition and destruction of their surfaces being the result of different after growth thermal, mechanical and chemical treatment. $Cd_{1-x}Mn_xTe$ mixed crystals are a class of AII-BVI semi-magnetic semiconductors which contain transition metal ions Mn in the Cd cation sites. This group of materials is promising as by varying Mn concentration it is possible to tune the fundamental band gap value in the range from 1.5 eV to 2.5 eV [1,2]. The main question in this paper was what other changes are caused by Mn admixture apart from the shift of the energy gap value. One of the issues of interest was the uniformity of composition of crystals grown with the admixture of Mn ions and the compositional broadening of the optical absorption band for the energy of photons below the energy gap value in so called Urbach edge region. All the numerical computations of the PPT spectra presented in this paper were performed in a modified Jackson & Amer [3] and Blonskij et.al [4] models, with a different temperature spatial distribution formula [5]. Results of preliminary computations of the PPT spectra indicated that it was not possible to reproduce experimental PPT spectra in a single layer model of samples. Finally the spectra were computed for different multi-layer models of real samples [6-8] and this approach turned out to be successful indicating the complex physical structure of

investigated samples. The fitting procedures were applied to determine the parameters characterizing the samples. For all investigated mixed crystals the following parameters were determined: E_g, β_0, γ and A_0 . These parameters are necessary for description of the optical absorption coefficient spectrum in the whole range of exciting photons. The formulae taken for computations were given by the expressions below:

For $E_{exc} < E_g$ $\beta(h\nu) = \beta_0 \cdot \exp\left((E_{exc} - E_g) \cdot \gamma / k \cdot T\right)$ (1)

For $E_{exc} > E_g$ $\beta(h\nu) = A_0 \cdot \sqrt{E_{exc} - E_g} + \beta_0$ (2)

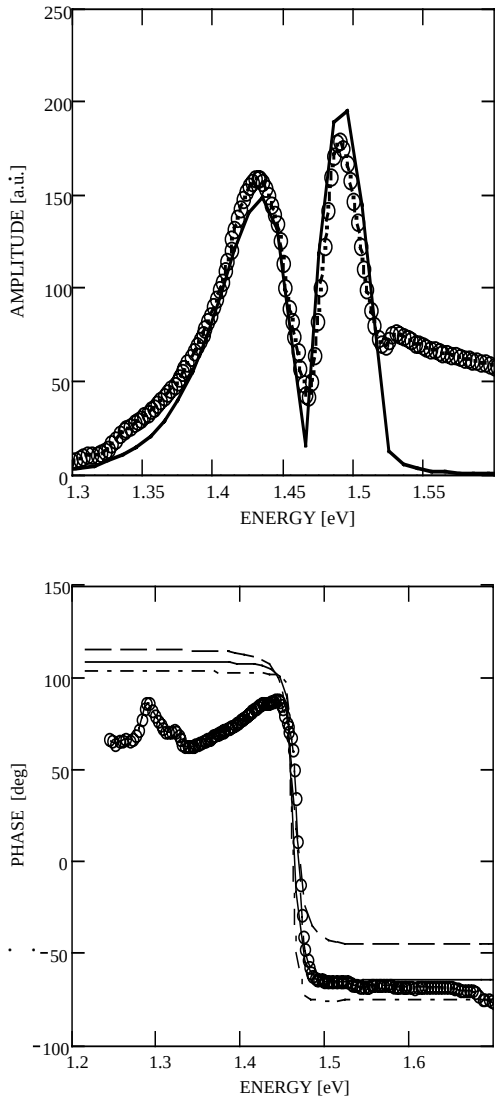
II. Experiment.

$Cd_{1-x}Mn_xTe$ mixed crystals were grown by the high pressure , high temperature Bridgman method [9]. The investigated crystals had an average Mn content of: x=0, 0.27, 0.49, 0.67. The PPT spectra were measured in the rear excitation configuration in the open acoustic cell with the phase sensitive detection [1]. All measurements were performed at room temperature.

III. Results and discussion.

The photoacoustic (PA) technique has already been applied for investigations of CdTe crystals with the piezoelectric detection [10,11] as also with the microphone one for
$Cd_{1-x}Mn_xTe$ [12]. It was expected, among others, that PA experiments could yield information about the quality and composition of samples.

Piezoelectric photothermal (PPT) amplitude and phase spectra of CdTe crystals measured at room temperature for the modulation frequency of *f=76 Hz* and the thickness of samples *l=0.1 cm* are shown in Fig.1.



a) b)

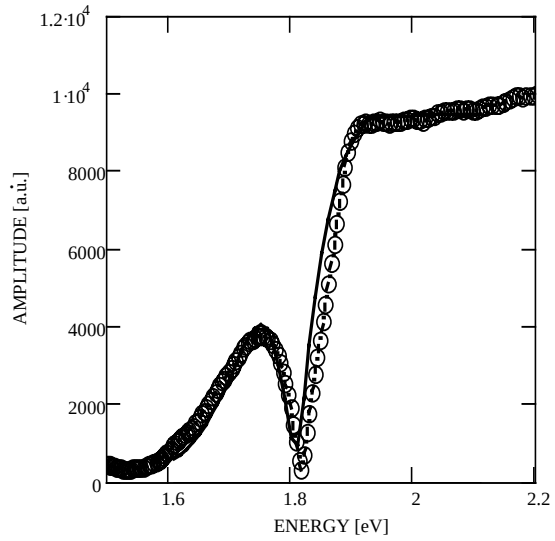
Fig.1. a) Amplitude PPT spectra of CdTe crystals at RT , *f=76 Hz*. Fitting parameters: E_g*=1.51 eV,* β_0*=130 cm*$^{-1}$*,* γ*=0.9,* α*=0.03 cm*^{2}*/s,* Δ*=0.019 cm.* Circles- experimental results,
solid line- theoretical curve.

b) Phase PPT spectra of CdTe crystals at RT, *f=76 Hz.* Circles- experimental results, lines- theoretical curves cumputed for dash line-α=0.2 cm^2/s, solid line-α*=0.10 cm*^{2}*/s,* dadot line-α*=0.05 cm*^{2}*/s R= -0.6.* All the rest parameters identical as for the amplitude spectra.

Computations of the spectra were performed for an inactive layer model. CdTe samples exhibited the value of the energy gap E_g*=1.51 eV* close to the literature data E_g*=1.5 eV* at RT.
Investigated crystal samples exhibited damages of the surface that were described by the thickness of an inactive layer Δ*=0.019 cm.* The phase spectra indicated the value of the

thermal diffusivity α in the range *0.05-0.1 cm^2/s.* The literature value is about *0.03 cm^2/s.* The PPT amplitude spectrum exhibited two peaks at 1.425 eV (low absorption peak) and 1.5 eV (high absorption peak). Computer analysis of the spectra led to the conclusion that none of the peaks is connected with any electron levels below the energy gap of CdTe. The high energy peak is the result of the surface damage of CdTe samples and its position depends on the mechanical treatment of the surface. The thickness of the damaged layer in the case of the presented above spectrum equals to Δ*=0.019 cm.* This layer, called an inactive layer, is a trap for thermal waves that are originally generated in its region and they do not bring contribution to the total piezoelectric spectrum. The peak observed in the low absorption region is only the result of the rear configuration applied when the measured signal is the difference of the thermal expansion and thermal bending contributions.

$Cd_{0.73}Mn_{0.27}Te$ mixed crystals doped with Mn ions during growth exhibited PPT spectra presented in Fig.2.



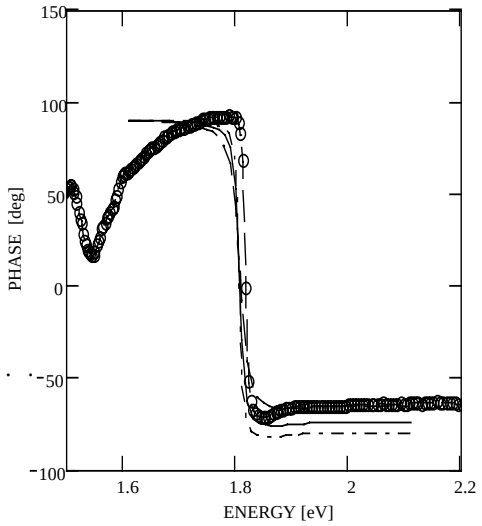
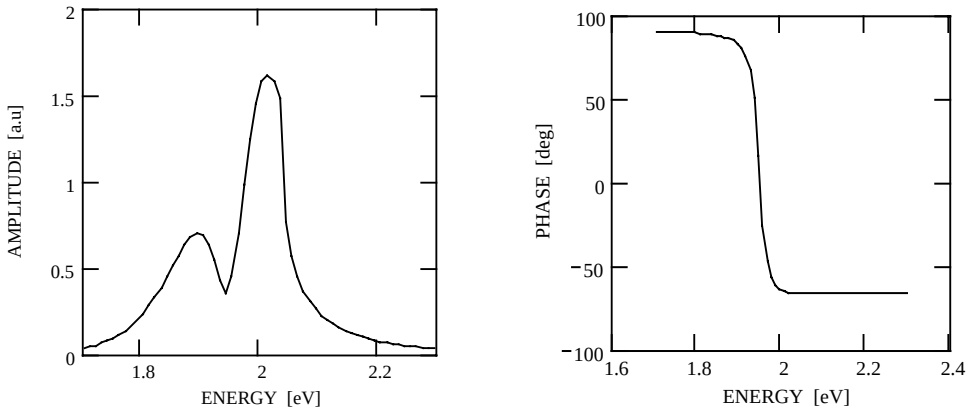


Fig.2. a) Amplitude PPT spectra of $Cd_{0.73}Mn_{0.27}Te$ mixed crystals measured at *f=76 Hz*, the thickness of samples was *l=0.15 cm*. The fitting parameters: *Eg=1.91 eV*, $\beta_0=150\ cm^{-1}$, $\gamma=0.5$, $\alpha=0.1\ cm^2/s$, *R=1*, $\Delta=0\ cm$. Circles- experimental results ,solid line- theoretical curve.

b) Phase PPT spectra of the same sample. The same fitting parameters were applied for the computations of theoretical curves. Circles – experimental results. Description of lines: dash-α=0.2 cm^2/s, solid -α=0.10 cm^2/s, dadot -α=0.05 cm^2/s, R= 1.

Computations in this case were performed for a single layer model. Doping of CdTe crystals with manganese at the concentration *x=0.27* ($Cd_{0.73}Mn_{0.27}Te$) caused a shift of the energy gap E_g from *1.51 eV* to *1.91 eV*. Mixed crystals $Cd_{0.73}Mn_{0.27}Te$ exhibited smaller thickness of an inactive layer equal in practice to $\Delta=0\ cm$. Phase spectra show also increase of the thermal diffusivity of the samples. Further increase of manganese concentration in the crystals generated different types of inhomogeneous in its spatial distribution in the investigated samples described below. Amplitude and phase PPT spectra of the mixed crystals $Cd_{0.51}Mn_{0.49}Te$ measured at RT and f=76 Hz are presented below in Fig.3. PPT spectra of these samples showed two kinds of crystal regions exhibiting energy gaps: $E_{g1}=2.035\ eV$ and $E_{g2}=2.105\ eV$ and different thickness of an inactive layer Δ=0.005 cm and Δ=0 cm.

Results of the analysis of the amplitude and phase PPT spectra of the above mentioned crystals are presented in Fig.3.a-f.



a) b)

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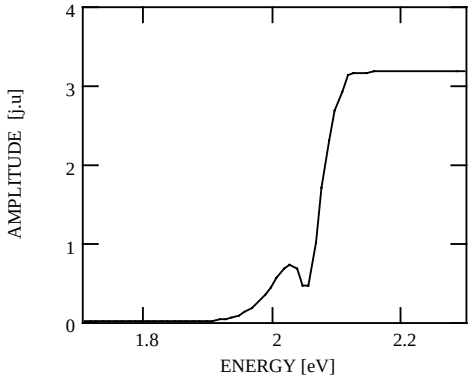
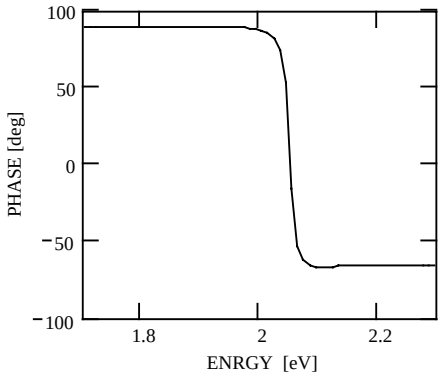
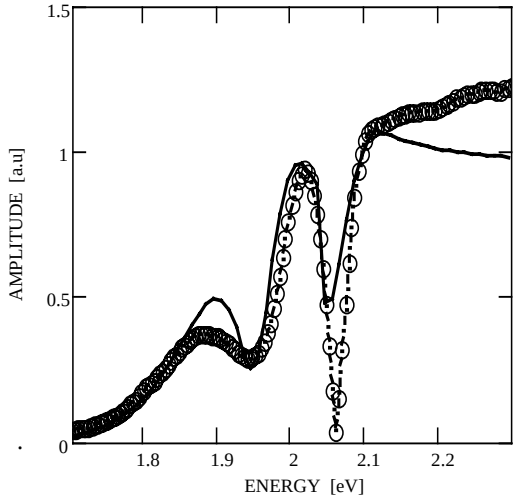
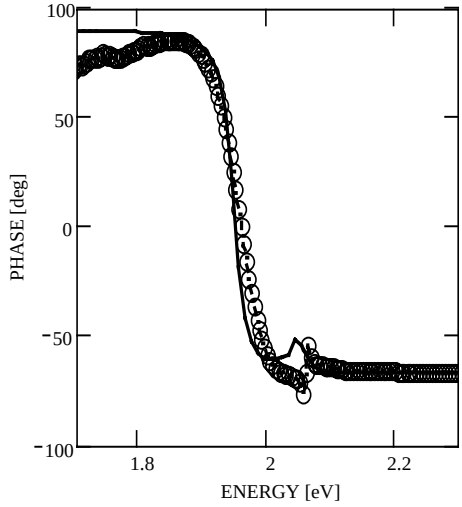

AMPLITUDE [j.u]
4
3
2
1
0
1.8
2
2.2
ENERGY [eV]


PHASE [deg]
100
50
0
−50
−100
1.8
2
2.2
ENRGY [eV]

c)

d)



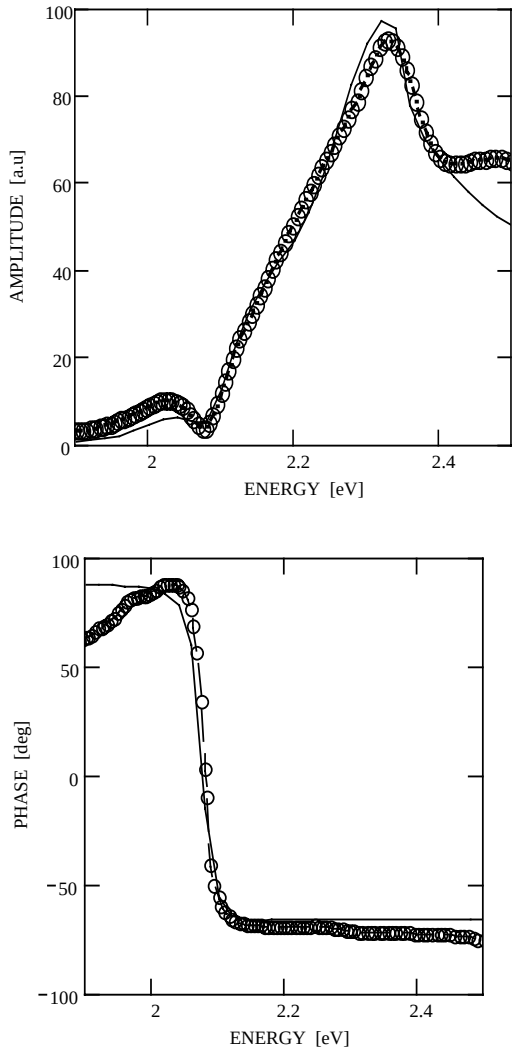


e) f)

Fig.3. Fitting parameters: : E_{g1}=2.035 eV, β_{01}=130 cm^{-1},γ_1=0.5, A_{01}=1500E_{g2}=2.105 eV, β_{02}=150 cm^{-1},γ_2=0.9,A_{02}=1500, α=0.1 cm^2/s, f=76 Hz, Δ_1=0.005 cm, Δ_2=0cm. R=1, k=0.3.
a) Theoretical amplitude and b) phase spectrum of the first crystal region : *E_{g1}=2.035 eV* and *Δ=0.005 cm.*
c) Theoretical amplitude and d) phase spectrum of the crystal region: *E_{g2}=2.105 eV* and *Δ=0 cm.*
e) Resulting theoretical amplitude and f) phase spectrum of $Cd_{0.51}Mn_{0.49}Te$ mixed crystal computed in a model of a superposition for k=0.3. Circles-experimental results, solid lines- theoretical curves.

Computations of the spectra were performed for a model of superposition of two PPT signals. In this model it is assumed that the PPT signal is a superposition of two signals coming from two independent crystal regions with the weighing factor described by a parameter *k.* Theoretical PPT spectra of the two crystal regions and the

resulting spectrum of the sample are all presented in Fig.3. Further increase of manganese concentration caused another qualitative change of the character of the spatial distribution of manganese in the samples. The analysis of the PPT spectra of $Cd_{0.33}Mn_{0.67}Te$ mixed crystals is presented in Fig. 4 a,b.



a) b)

Fig.4. Amplitude a) and phase b) PPT spectra of $Cd_{1-x}Mn_xTe$ mixed crystals for x=0.67 , *l*=0.1, f=76Hz. Fitting parameters: $E_{g1}=2.16$ *eV*, $E_{g2}=2.34$ *eV*, $\gamma_1=0.5$, $\gamma_2=0.5$, $\beta_{o1}=150\ cm^{-1}$, $\beta_{o2}=150\ cm^{-1}$, $\Delta_1=0.0017$*cm*, $\Delta_2=0.020$*cm*, $\alpha=0.1$, $R=1$. Circles- experimental results, solid line- theoretical curve.

Amplitude PPT spectrum proved the existence of two different crystal regions exhibiting energy gaps: $E_{g1}=2.16$ *eV and* $E_{g2}=2.34$ *eV* respectively. Computations of the spectra were performed for a model of an enriched layer. Crystal regions exhibiting different values of energy gaps are placed in a layer configuration described in detail for a model of the enriched layer. In this model it is assumed that the concentration of

manganese in the upper layer of the sample of the thickness of about $\Delta_2=0.020\ cm$ is greater than in the interior of the sample what results in the bigger value of its energy gap equal to $E_{g2}=2.34\ eV$. The thickness $\Delta_1=0.0017cm$ means the thickness of an inactive layer. The inactive layer is the uppermost layer of the sample in this model. It is responsible for the decrease of the amplitude of PPT signal for the photon energies above 2.3 eV (see Fig.4a).

Spectral analysis presented above enabled the percentage estimation of the composition of samples. This analysis was possible thanks to the calibration characteristic shown in Fig.5. It presents the dependence of the energy gap value of the $Cd_{1-x}Mn_xTe$ mixed crystals on the concentration of manganese.

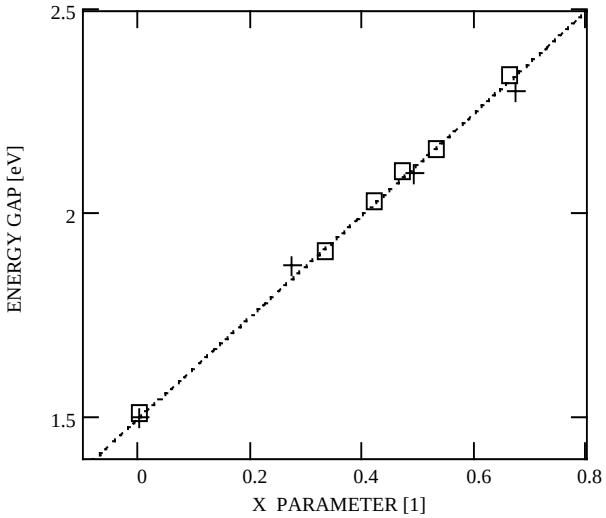


Fig.5. Dependence of the energy gap value E_g on the x parameter describing manganese concentration in the $Cd_{1-x}Mn_xTe$ crystal sample. Crosses denote values of the x parameter presented in [2]. Squares denote values of energy gaps extracted from the analysis of the PPT spectra of investigated samples.

Application of multi-layer models in the numerical analysis of the amplitude and phase PPT spectra enabled the determination of the percentage composition of the samples. Results of computations are presented in Table 1.

Table1. Percentage composition determined from the PPT spectra.

Parameter X	Percentage composition I crystal region	Percentage composition II crystal region
0	CdTe 100 %	----------
0.27	$Cd_{0.67}Mn_{0.33}Te$ 100%	----------
0.49	$Cd_{0.58}Mn_{0.42}Te$ 70%	$Cd_{0.53}Mn_{0.47}Te$ 30%
0.67	$Cd_{0.47}Mn_{0.53}Te$ 60%	$Cd_{0.34}Mn_{0.66}Te$ 40%

IV. Conclusions.

Results of the analysis of piezoelectric spectra of mixed crystals $Cd_{1-x}Mn_xTe$ indicated that their composition exhibits non-uniform character. The need of explanation of the characteristic features of the observed PPT spectra brought about the

application of a few multi-layer models. For the numerical description of the PPT spectra the following models were applied: single layer model for x=0.27, an inactive layer model for x=0, a model of superposition for x=0.49 and an enriched layer model for x=0.67. These models reflect the complexity of physical structure of analyzed samples. Application of these models enabled the determination of the percentage composition of crystals and the set of basic optical parameters. The computations of the phase spectra enabled determination of the thermal diffusivities of samples without the necessity of separate frequency domain experiments.

References.

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